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### **JAPANESE / ENGLISH TRANSLATION OF**

Japanese Patent Application JP 2003 - 201391 A

Polyester Resin Composition for Calendering, and Sheet Obtained Using This Composition

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For: Eastman Chemical Company

9109 Eagle Hills Dr . Las Vegas NV 89134 . ph: 866-722-7990 (toll-free) . fax: 702-973-6009 . email: sales@tls-translations.com

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| (21) Applic                | cation No.:     | P2002-819       |           | (71)    | Applicant: | 000003160   |
| (22) Filing                | Date:           | January 7, 2002 |           |         | -          | ., Ltd.; 2-8, Doshima Hama 2<br>a-ku, Osaka-shi, Osaka-fu     |
|                            |                 |                 |           | (72)    | Inventor:  | Kazunori Komatsu  |
|                            |                 |                 |           |         |            | Co., Ltd., Research Center, 1-1, nome, Otsu-shi, Shiga-ken    |
|                            |                 |                 |           | (72)    | Inventor:  | Osamu Iritani   |
|                            |                 |                 |           |         |            | Co., Ltd., Research Center, 1-1,<br>nome, Otsu-shi, Shiga-ken |
|                            |                 |                 |           | (72)    | Inventor:  | Mitsuo Nishida  |
|                            |                 |                 |           |         |            | Co., Ltd., Research Center, 1-1, nome, Otsu-shi, Shiga-ken    |
|                            |                 |                 |           | (72)    | Inventor:  | Tsuyoshi Hachitsuka   |
|                            |                 |                 |           |         | •          | Co., Ltd., Research Center, 1-1, nome, Otsu-shi, Shiga-ken    |
|                            |                 |                 |           |         |            | (Continued on last page)                                      |

#### (54) [Title of the Invention]

Polyester Resin Composition for Calendering, and Sheet Obtained Using This Composition

#### (57) [Summary]

[Object] To provide a polyester resin composition with good roll release properties during calendering and to allow high-quality calendering to be performed such that the resulting sheet has good transparency and excellent solvent resistance and detergent resistance.

[Means of Achievement] The invention relates to a polyester composition for calendering wherein 0.01 to 5 parts by weight of crystal nucleator and 0.01 to 5 parts by weight of lubricant are admixed per 100 parts by weight of crystalline polyester with a melting point of 200°C or lower. The invention preferably relates to a polyester resin for calendering wherein this crystal nucleator is a fatty acid salt.

#### [Claims]

[Claim 1] A polyester resin for calendering, characterized in that 0.01 to 5 parts by weight of crystal nucleator and 0.01 to 5 parts by weight of lubricant are admixed per 100 parts by weight of crystalline polyester with a melting point of 200°C or lower.

[Claim 2] The polyester resin for calendering according to claim 1, characterized in that the crystal nucleator is a fatty acid salt.

[Claim 3] The polyester resin for calendering according to claim 2, characterized in that the crystal nucleator is the sodium salt of a fatty acid.

[Claim 4] The polyester resin composition for calendering according to any of claims 1 through 3, characterized in comprising 50 mol% or more of at least one of ethylene glycol,

1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and 1,4-cyclohexanedimethanol when the total glycol component of the crystalline polyester is taken to be 100 mol%.

[Claim 5] The polyester resin composition for calendering according to claims 1 through 4, characterized in that the crystalline polyester is a random copolymer.

[Claim 6] A sheet obtained by means of calendering the resin composition according to any of claims 1 through 5.

## [Detailed Description of the Invention] [0001]

[Technological Field of the Invention] The present invention relates to a polyester resin composition that has excellent roll release properties, long-run calenderability, and heat stability; is ideal for calendering; and is therefore useful for various sheets and films, including shrink labeling for food products, cosmetics, and beverages, aroma-retaining heat sealed film, oil-resistant multilayer sheets, and the like, particularly industrial sheets and films.

#### [0002]

[Prior Art] Vinyl chloride sheets (including film; the same hereafter) have often been used for a variety of purposes in the past because of their low cost and excellent transparency. Extrusion and calendering are known as methods of working these sheets. When compared to calendering, extrusion is less precise in terms of sheet thickness, width, the direction of flow, and the like because die lip friction determines resin workability (moldability), and extrusion is also unsuited for mass production. Thus, calendering is more often used from the viewpoint of productivity and quality. Moreover, flexibility can be controlled as needed as a result of adding a plasticizer to vinyl chloride, and, therefore, it can be easily molded into sheets. A typical example of the use of this sheet is as a decorative laminated sheet imprinted with a wood grain in order to enhance the design of wood. Nevertheless, in recent years there has been a trend toward replacing vinyl chloride sheets with other materials because of a variety of problems. Of the several substitutes, polyester is more effective in terms of its physical properties, cost, and the like. However, there are two major problems with replacing polyvinyl chloride with polyester. [0003] First, it is difficult to use polyester for calendering, which is often used as a method of molding vinyl chloride sheets. In the past, extrusion has been the primary method of making polyester resin sheets and film because it is easy to mold polyester resin by means of extrusion. By contrast, when polyester resin is calendered, there is relatively strong adhesion to the roll during plasticizing as a result of heating, and the resin is apt to deposit on the roll during calendering, making molding difficult. Therefore, attempts have been made to add a variety of lubricants in order to prevent adhesion to the roll. Studies of such lubricants have been conducted using hydrocarbon lubricants such as polyethylene wax and paraffin wax, higher fatty acid lubricants, higher alcohol lubricants, metallic soaps from higher fatty acids, fatty acid amide lubricants, ester lubricants, and various other lubricants, but it is still impossible to ensure adequate roll release properties and long-run time, and there are problems in that the resulting sheet (film) is discolored and the hue of the sheet (film) is adversely affected with long-run calendering.

[0004] The second problem is the low resistance to chemical products such as solvents and detergents, and the resin turns white and swells when immersed in or scrubbed with these chemical products. When wood to which a laminated sheet has been glued is made into tables and furniture or cabinet doors, the sheet tends to become stained. When an attempt is made to

wipe the sheet with a solvent such as alcohol or methyl ethyl ketone in order to remove the stains, the polyester itself crystallizes and turns white, or swells without crystallizing, resulting in an appearance that has deteriorated to the point that it cannot be used. Moreover, in households and kitchens, stains are removed using solvents on a daily basis, and using such furniture in the ordinary home is problematic in that the appearance is eventually affected in the same way as when the furniture is wiped with a solvent.

[0005] Examples of previous studies on the calendering of polyester resins are shown below, and prior art is described in further detail. Amorphous polyethylene terephthalate copolymerized with cyclohexanedimethanol is made into sheets by means of calendering in JP (Kokai) 11-343353, JP (Kokai) 2000-136294, JP (Kokai) 2000-186191, JP (Kokai) 2000-302951, JP (Kokai) 2001-64496, JP (Kokai) 2001-4019, and US-6068910, and although adequate transparency is obtained, chemical resistance is always insufficient, with the sheet turning white when it is immersed in a solvent, making its practical use as a laminated sheet difficult. In addition, when the calendering test disclosed by the inventors was performed, there was a reduction in sheet transparency and printability after calendering when the amount of lubricant was increased, while the ease of release from the rolls during molding decreased when the amount of solvent was reduced, making it impossible to strike a balance between the two properties. Another drawback is that when these lubricants were used as principal components, the sheet gradually discolored during long-run calendering, and the sheet appearance deteriorated.

#### [0006]

[Problems to Be Solved by the Invention] The present invention, which was perfected in light of the above-mentioned facts, is aimed at providing a polyester resin composition for calendering that allows adequate roll release properties during calendering and improved sheet properties after calendering (virtually no discoloration, good transparency and printability, and excellent solvent resistance and detergent resistance) to be realized at the same time.

#### [0007]

[Means Used to Solve the Above-Mentioned Problems] The inventors performed intense studies to accomplish the above-mentioned object, and, as a result, they completed the present invention upon discovering that it is possible to ensure that adequate roll release properties and long-run processing properties during calendering, as well as improved sheet properties after

calendering (virtually no discoloration, good transparency and printability, and excellent solvent resistance and detergent resistance) can be simultaneously obtained as a result of mixing together a crystalline polyester that has a melting point of 200°C or lower, a crystal nucleator, and a lubricant.

[0008] That is, the present invention is characterized as follows.

- (1) A polyester resin for calendering characterized in that 0.01 to 5 parts by weight of crystal nucleator and 0.01 to 5 parts by weight of lubricant are admixed per 100 parts by weight of crystalline polyester with a melting point of 200°C or lower.
- [0009] (2) The polyester resin for calendering according to (1), characterized in that the crystal nucleator is a fatty acid salt.
- [0010] (3) The polyester resin for calendering according to (2), characterized in that the crystal nucleator is the sodium salt of a fatty acid.
- [0011] (4) The polyester resin composition for calendering according to any of (1) through (3) characterized in comprising 50 mol% or more of at least one of ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and 1,4-cyclohexanedimethanol when the total glycol component of the crystalline polyester is taken to be 100 mol%.
- [0012] (5) The polyester resin composition for calendering according to (1) through (4), characterized in that the crystalline polyester is a random copolymer.
- [0013] (6) A sheet obtained by means of calendering the resin composition according to any (1) through (5).

#### [0014]

[Embodiments of the Invention] The polyester resin composition for calendering in accordance with the present invention is characterized in that 0.01 to 5 parts by weight of crystal nucleator and 0.01 to 5 parts by weight of lubricant are admixed per 100 parts by weight of crystalline polyester with a melting point of 200°C or lower. The characterizing feature of this composition is that it is possible to simultaneously obtain excellent roll release properties and long-run processing properties during calendering, as well as improved sheet properties after calendering (virtually no discoloration, good transparency and printability, and excellent solvent resistance and detergent resistance).

[0015] The polyester used in the present invention must be crystalline. The term "crystalline" used here means that the polyester shows a melting peak as measured using a differential scanning calorimeter (DSC) during a two-step temperature-increasing process whereby the temperature is first raised from -100°C to 300°C at 20°C/min, then reduced to -100°C at 50°C/min, and subsequently raised again from -100°C to 300°C at 20°C/minute. Conversely, the term "amorphous" means that there is no obvious melting peak during either of the temperatureincreasing steps. The polyester that is used in the present invention must be crystalline, and, therefore, there is a melting peak. The melting point of the crystalline polyester resin used in the present invention must be 200°C or lower. The melting point is preferably 190°C or lower, particularly 180°C or lower, and ideally 170°C or lower. On the other hand, although there are no special restrictions to the lower limit, this limit is commonly 90°C or higher, preferably 100°C or higher, particularly 120°C or hither, and ideally 130°C or higher, if heat resistance and the like are taken into consideration. If the melting point is lower than 90°C, there will be a reduction in crystallinity, and, as a result, solvent resistance and detergent resistance will decline. On the other hand, if the melting point exceeds 200°C, it will be necessary to set a higher roll surface temperature for calendering, and, therefore, there will be a reduction in molecular weight due to hydrolysis of the polyester, and, consequently, the roll release properties during calendering will be adversely affected and there will be a reduction in sheet elongation. [0016] The glass transition temperature of the crystalline polyester resin used in the present invention should be -100 to 70°C. The preferred lower limit is -80°C, and particularly -70°C. An even more preferred upper limit is 60°C. If the glass transition temperature is less than -100°C, there may be cases in which the resulting sheet will show strong tackiness and the sheets will readily block one another, which is undesirable. On the other hand, if a crystalline polyester resin whose glass transition temperature exceeds 70°C is used, there is a chance that the sheet will suddenly cool at room temperature during the post-calendering cooling step and that crystallization of the crystalline polyester resin will not proceed to its fullest, resulting in a reduction in solvent resistance.

[0017] The crystalline polyester used in the present invention is preferably a random copolymer. The term "random polymer" used here means, for instance, a polymer other than an elastomer-type block copolymer containing both soft segments and hard segments in its molecules.

Specifically, it is a polyester other than one in which a polycaprolactone component been introduced into the main chain of the polyester as a result of the ring-opening addition polymerization of ε-caprolactone or the like, or one in which polyethylene glycol such as polyethylene glycol, polytetramethylene glycol, polypropylene glycol has been copolymerized as the soft segment. When a soft segment is present within the molecules, the solvent resistance of this portion is poor and the resulting sheet will turn white and swell when immersed in a solvent such as methyl ethyl ketone, acetone, or toluene. In other words, as long as the copolymer is a fully random copolymer with no soft segments in block form within the molecules, the crystal state of the copolymer will be uniform on the molecular level, and, therefore, excellent solvent resistance will be realized. The crystalline polyester used in the present invention should comprise 50 mol% or more of at least one of ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and 1,4-cyclohexanedimethanol when the total glycol component is taken to be 100 mol%. The preferred amount is 55 mol% or more, particularly 60 mol% or more. It is important that the crystalline polyester present in the sheet be rapidly crystallized in order to ensure the desired solvent resistance, and this polyester should account for 50 mol% or more of the above-mentioned component in order to provide sufficient crystallinity. If this amount is less than 50 mol%, there is a chance that there will be a reduction in solvent resistance. Of the above-mentioned components, the use of 1,3-propanediol and 1,4-butanediol is particularly preferred from the standpoint of solvent resistance because crystallization will proceed quickly. [0018] The crystalline polyester resin that is used in the present invention can be a copolymer with a polycarboxylic acid component or polyhydric alcohol component other than the abovementioned ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and 1,4-cyclohexane dimethanol. It is possible, for instance, to use a well-known polycarboxylic acid component such as terephthalic acid, isophthalic acid, orthophthalic acid, naphthalene dicarboxylic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, decanoic acid, dimer acid, cyclohexanedicarboxylic acid, and trimellitic acid. It is also possible to use a polyhydric alcohol component such as 1,2-butanediol, 1,3-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 2-methyl-1,3-propanediol, nonanediol, dimer diol, ethylene oxide adduct or propylene oxide adduct of bisphenol A, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, 2-butyl-2-ethyl-1,3-propanediol, tricyclodecane dimethanol, neopentyl hydroxypivalic acid ester, 2,2,4-trimethyl-1,5-pentanediol, trimethylol propane, or the like.

[0019] The number-average molecular weight of the crystalline polyester resin used in the present invention is preferably 15,000 to 40,000, particularly 18,000 to 35,000, and ideally 20,000 to 35,000. If the number-average molecular weight is less than 15,000, strength and elongation are inadequate due to inadequate resin cohesion, making the resin brittle and unusable. On the other hand, if this molecular weight becomes 40,000 or higher, there is a chance that melt viscosity will rise and the optimum temperature for calendering will also increase, resulting in deterioration of roll release properties.

[0020] The acid value of the crystalline polyester resin used in the present invention is preferably  $60 \text{ eq}/10^6 \text{ g}$  or less, particularly  $50 \text{ eq}/10^6 \text{ g}$  or less, and ideally  $40 \text{ eq}/10^6 \text{ g}$  or less. If the acid value exceeds  $60 \text{ eq}/10^6 \text{ g}$ , there will be cases where hydrolysis will be further accelerated when the resin is heated during calendering, and there will be a reduction in mechanical strength of the resulting sheet. In addition, there will be cases in which roll release properties will also decrease as a result of resin decomposition.

[0021] When measured at a temperature of 220°C and a shear speed of 100 sec<sup>-1</sup>, the melt viscosity of the polyester resin composition used in the present invention is preferably 6,000 to 60,000 dPa·sec, particularly 7,000 to 50,000 dPa·sec, and ideally 8,000 to 40,000 dPa·sec. If the melt viscosity is less than 6,000 dPa·sec, the roll release properties will be adversely affected because there will be an increase in resin tackiness. On the other hand, increasing the melt viscosity above 60,000 dPa·sec is sometimes impractical because melt viscosity is too high and the productivity is reduced.

[0022] Examples of methods for determining the composition and the compositional ratio of the polyester resin used in the present invention (as well as the composition and the compositional ratio of the polyester resin composition) include <sup>13</sup>C-NMR and <sup>1</sup>H-NMR (in which the polyester resin is measured after dissolution in a solvent such as heavy chloroform), as well as gas chromatography, in which the polyester resin is measured after being subjected to methanolysis. Of these, <sup>1</sup>H-NMR is preferred because of its simplicity.

[0023] When a sheet is produced by means of calendering the polyester resin of the present invention, it is necessary to admix a lubricant into this polyester resin in order to improve its roll release properties.

[0024] The amount of lubricant used in the present invention is 0.01 to 5 parts by weight. The preferred lower limit is 0.05 part by weight, the particularly preferred lower limit is 0.1 part by

weight, and the ideal lower limit is 0.5 part by weight. The preferred upper limit is 4.5 parts by weight, the particularly preferred upper limit is 4 parts by weight, and the ideal upper limit is 3.5 parts by weight. If the amount of lubricant is less than 0.01 part by weight, it will be difficult to improve the roll release properties, while if this amount exceeds 5 parts by weight, the sheet obtained by means of calendering will tend to lose some of its transparency, to undergo discoloration, and to become less suitable for printing.

[0025] There are no special restrictions to the lubricant used in the present invention. Examples include polyolefin waxes, metal salts of organic phosphoric acid esters, organic phosphoric acid esters, ester compounds of adipic acid or azelaic acid and higher aliphatic alcohols, fatty acid amides (such as ethylene bis-stearic acid amide, methylene bis-stearic acid amide, and ethylene bis-oleic acid amide), glycerin higher fatty acid ester compounds, pentaerythritol higher fatty acid ester compounds, higher aliphatic alcohols, higher fatty acids, metallic soaps from higher fatty acids, and paraffin, waxes, and natural or synthetic polymer ester waxes derived from petroleum or coal. One of these can be used, or two or more can be used together. [0026] It is necessary to add 0.01 to 5 parts by weight of crystal nucleator to the polyester resin composition of the present invention. The preferred lower limit is 0.05 parts by weight and the particulary preferred lower limit is 0.1 part by weight. On the other hand, the preferred upper limit is 4 parts by weight and the particularly preferred upper limit is 3.5 parts by weight. The crystal nucleator has the effect of increasing the speed of crystallization of the crystalline polyester to allow crystallization to be rapidly completed, and of making it possible to control the spherulite size by means of adjusting the number of crystal nuclei. That is, sheet transparency and solvent resistance can be improved at the same time as a result of adjusting these factors. Specific examples of crystal nucleators include inorganic fine particles such as talc, silica, graphite, carbon powder, pyroferrite, gypsum, and neutral clay; and metal oxides such as magnesium oxide, aluminum oxide, and titanium dioxide; as well as sulfates, phosphates, silicates, oxalates, stearates, benzoates, salicylates, tartrates, sulfonates, montanic acid wax salts, montanic acid wax ester salts, terephthalates, carboxylates, and ionic copolymers of  $\alpha$ -olefins and  $\alpha,\beta$ -unsaturated carboxylates. Of these, metal salts such as zinc salts, calcium salts, magnesium salts, sodium salts, and lithium salts of fatty acids such as hexanoic acid, lauric acid, stearic acid, and montanic acid are preferred because they make it easier to adjust the

crystallization speed. When a sodium salt of a fatty acid in particular is used, it is easy to control the spherulite size, and a transparent sheet can be produced with ease.

[0027] It is preferred that a composition be used wherein an antioxidant has been admixed with the polyester resin of the present invention in order to control the thermal degradation of the polyester resin during calendering (to prevent resin discoloration, roll adhesion, and other phenomena associated with thermal degradation). Phenol antioxidants and organic phosphorous acid ester compounds are ideal as this type of antioxidant.

[0028] The maximum amount of antioxidant is preferably 1.0 parts by weight or less, and particularly 0.8 part by weight or less. The lower limit is preferably 0.01 part by weight or more, and particularly 0.02 part by weight or more. If the amount is less than 0.01 part by weight, it will be difficult to achieve the effect of controlling thermal degradation during calendering, while an amount in excess of 1.0 part by weight is not economical because the effect of controlling thermal degradation will be saturated.

[0029] The joint use of a phenol antioxidant and organic phosphorous acid ester is preferred because the effect of controlling thermal degradation is further enhanced.

[0030] Other resins can be blended as needed with the polyester resin composition of the present invention as long as the amounts blended are within a range that does not compromise the performance of the composition. Other polyester resins, epoxy resins, polyamide resins, acrylic resins, polycarbonate resins, polystyrene resins, and polyolefin resins (such as polyethylene resins and polypropylene resins) can be added as needed. Other components can also be added as needed to the polyester resin composition of the present invention. Fillers, ultraviolet absorbers, photostabilizers, pigments, antistatics, antibacterial agents, epoxy compounds, crosslinking agents, and sulfur antioxidants can be cited as examples.

#### [0031]

[Working Examples] Working examples are cited below in order to describe the present invention in further detail, but the present invention is in no way limited to the working examples. The measurements cited in the synthesis examples were obtained in accordance with the following methods.

[0032] Resin composition: The resin was dissolved in heavy chloroform and assayed by means of <sup>1</sup>H-NMR.

[0033] Glass transition temperature, melting point: Measured at a temperature increase rate of 20°C/min using a differential scanning calorimeter after placing a 10 mg of sample in an aluminum pan and pressing the lid closed.

[0034] Number-average molecular weight: Found as the value in terms of polystyrene by means of gel permeation chromatography using hexafluoroisopropanol as a solvent.

[0035] Acid value: Found by means of the dissolution of resin in chloroform and titration with a 0.1 N potassium hydroxide-ethanol solution. Phenolphthalein was used as the indicator.

[0036] <Polyester (A) synthesis example>

141 parts by weight of dimethyl terephthalate, 25 parts by weight of dimethyl isophthalate, 87 parts by weight of ethylene glycol, 54 parts by weight of butanediol, and 0.07 weight part of tetrabutyl titanate were placed in a reactor equipped with a stirrer, thermometer, and a distillate cooler, and transesterification was performed for two hours at 170 to 220°C. Once transesterification was completed, the temperature of the reaction system was raised from 220°C to 250°C as the pressure inside the system was gradually reduced to 500 Pa over a 60-minute period. Polycondensation was then performed for 55 minutes at 130 Pa or below to obtain polyester (A).

[0037] According to NMR analysis of amorphous polyester (A), the dicarboxylic acid component had a composition of 85 mol% of terephthalic acid and 15 mol% of isophthalic acid, and the diol component had a composition of 49 mol% of ethylene glycol and 51 mol% of butanediol. The glass transition temperature was 49°C, the melting point was 177°C, the number-average molecular weight was 28,000, and the acid value was 30 eq/10<sup>6</sup> g. Polyesters (B) through (F) were manufactured in the same manner as polyester (A). The compositions and measurement results are shown in Table 1. (The numbers are mol% of the resin.)

[0038]

[Table 1]

|            |                                   | Polyester synthesis examples |        |        |        |        |          |  |
|------------|-----------------------------------|------------------------------|--------|--------|--------|--------|----------|--|
|            |                                   | Α                            | В      | С      | D      | Е      | F        |  |
|            | Terephthalic acid                 | 85                           | 63     | 83     | 100    | 91     | 100      |  |
| Acid       | Isophthalic acid                  | 15                           | 12     |        |        | 9      |          |  |
|            | Adipic acid                       |                              | 25     | 17     |        |        |          |  |
| Glycol     | Ethylene glycol                   | 49                           |        | 33     | 26     |        | 70       |  |
|            | 1,3-Propanediol                   |                              |        | 77     |        |        | <u> </u> |  |
|            | 1,4-Butanediol                    | 51                           | 100    |        |        | 100    | <u> </u> |  |
|            | 1,4-Cyclohexane dimethanol        |                              |        |        |        |        | 30       |  |
|            | 1,6-Hexanediol                    |                              |        |        | 74     |        | <u> </u> |  |
| Properties | Number-average molecular weight   | 28,000                       | 24,000 | 21,000 | 33,000 | 25,000 | 30,000   |  |
|            | Glass transition temperature (°C) | 49                           | -6     | 45     | -5     | 25     | 78       |  |
|            | Melting point (°C)                | 177                          | 163    | 158    | 175    | 211    | None     |  |
|            | Acid value (eq/10 <sup>6</sup> g) | 30                           | 26     | 18     | 12     | 32     | 18       |  |

#### [0039] Working Example 1

One-hundred parts by weight of crystalline polyester A, 1 part by weight of tridecyl poly(oxyethylene)phosphate zinc salt as a lubricant, and 1 part by weight of sodium stearate as a crystal nucleator were mixed in a beaker and kneaded on two 6-inch test rolls that were set to 180°C. The ingredients were mixed while the resin that adhered to the test rolls was occasionally peeled off with a spatula. After five minutes of kneading, the roll distance was set at 0.3 mm (sheet thickness setting of 0.3 mm) to obtain a sheet. The results are shown in Tables 2 and 3.

[0040] The lubricant and nucleator cited in Tables 2 and 3 are defined below.

I: Tridecyl poly(oxyethylene)phosphate zinc salt

II: Styrene-modified polyethylene wax

III: Sodium stearate

IV: Sodium montanic acid salt

Moreover, the amounts of polystyrene, lubricant, and nucleator in the table are shown as parts by weight.

## [0041]

## [Table 2]

|            |                    |     |     | Worl | king Exam | ples |    |     |
|------------|--------------------|-----|-----|------|-----------|------|----|-----|
|            |                    | 1   | 2   | 3    | 4         | 5    | 6  | 7   |
|            | Α                  | 100 | 100 | 100  |           |      |    |     |
|            | В                  |     |     |      | 100       | 100  |    |     |
|            | С                  |     |     |      |           |      | 92 |     |
| Polyester  | D                  |     |     |      |           |      |    | 100 |
|            | E                  |     |     |      |           |      |    |     |
|            | F                  |     |     |      |           |      | 8  |     |
| T 1        | I                  | 1   | 1   | 1    | 1.2       | 0.8  | 1  | 1   |
| Lubricant  | II                 |     |     | 0.5  |           | 0.2  |    |     |
| Crystal    | III                | 1   |     | 1    | 1.2       | 1    | 1  |     |
| nucleator  | IV                 |     | 0.7 |      |           |      |    | 1.2 |
| Production | Transparency       | 5   | 4   | 5    | 5         | 5    | 4  | 4   |
| Evaluation | Solvent resistance | 5   | 5   | 5    | 4         | 4    | 5  | 5   |

## [0042]

[Table 3]

|                   |                    |                      |     |     |     | <del></del> |     |     |     | <del></del> |
|-------------------|--------------------|----------------------|-----|-----|-----|-------------|-----|-----|-----|-------------|
|                   |                    | Comparative Examples |     |     |     |             |     |     |     |             |
|                   |                    | 1                    | 2   | 3   | 4   | 5           | 6   | 7   | 8   | 9           |
|                   | Α                  | 100                  | 100 | 100 |     |             |     |     |     |             |
| Polyester         | В                  |                      |     |     | 100 |             |     |     |     |             |
|                   | С                  |                      |     |     |     |             | 100 |     |     |             |
|                   | D                  |                      |     |     |     | 100         |     |     |     |             |
|                   | Е                  |                      |     |     |     |             |     | 100 |     |             |
|                   | F                  |                      |     |     |     |             |     |     | 100 | 100         |
| T. I. Januar      | I                  |                      | 1   |     | 5.5 | 1           | 1   | 1   | 1   | 1           |
| Lubricant         | II                 |                      |     |     |     |             |     |     |     | 0.2         |
| Crystal nucleator | III                | 1                    |     |     | 1   | 5.8         |     |     | 1   |             |
|                   | IV                 |                      |     |     |     |             |     | 1.2 | _   |             |
| Evaluation        | Transparency       | -                    | 3   |     | 1   | 2           | 2   | ×   | 4   | 4           |
|                   | Solvent resistance | _                    | 2   | -   | 3   | 3           | 3   | 2   | 2   | 1           |

[0043] The methods of evaluating transparency and solvent resistance in the tables are as shown below.

Transparency: The sheets were compared macroscopically and evaluated according to the following criteria. (5: extremely transparent; 4: good transparency; 3: transparent; 2: slightly opaque; 1: opaque, ×: very poor sheet appearance with many small holes)

Solvent resistance: After being immersed for ten minutes in methyl ethyl ketone, the sheets were compared macroscopically for whitening and swelling and evaluated according to the following criteria. (5: no change; 4: some swelling, but no significant change; 3: turned white; 2: turned white and slightly swollen at the surface; 1: turned white and surface dissolved.)

The "-" in the comparative examples under the columns for evaluation of transparency and solvent resistance indicates that a sheet could not be made due to adhesion of the resin composition to the test roll.

#### [0044] Examples 2 through 7 and Comparative Examples 1 through 9

Evaluations were performed as described in Working Example 1 using the crystalline polyester cited in Table 1 and the lubricant and crystal nucleator cited in Tables 2 and 3. The results are shown in Tables 2 and 3.

[0045] Comparative Example 1 is outside the scope of the patent claims in that no lubricant is used. Comparative Example 2 is outside the scope of the patent claims in that no crystal nucleator is used. Comparative Example 3 is outside the scope of patent claims in that neither lubricant nor crystal nucleator is used. Comparative Example 5 is outside the scope of the patent claims in that the amount of lubricant is increased. Comparative Example 6 is outside the scope of the patent claims in that no crystal nucleator is added. Comparative Example 7 is outside the scope of the patent claims in that the melting point of the crystalline polyester is higher. Comparative Example 8 is outside the scope of the patent claims in that the polyester is amorphous. Comparative Example 9 is outside the scope of the patent claims in that the polyester is amorphous and no crystal nucleator is added.

[0046] As is clear from Tables 2 and 3, the compositions described in Working Examples 1 through 7 have excellent calenderability, transparency, and solvent resistance.

#### [0047]

[Effect of the Invention] As was previously described, the polyester resin composition of the present invention is a combination of a crystalline polyester with a melting point of 200°C or lower, a crystal nucleator, and a lubricant. The use of this composition not only facilitates calendering of polyester resin composition, which was impossible in the past, but also makes it possible to provide a high-quality calendered sheet with good transparency in the resulting sheet and with excellent solvent resistance and detergent resistance.

#### Continuation of front page

| (51) Int. Cl. <sup>7</sup> | Class. Symbols                              | FI           | Subject Codes (Reference) |
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| (72) Inventor:             | Kazunori Komatsu<br>c/o Toyobo Co., Ltd., C | entral       |                           |
|                            | Research Center, 1-1, K                     |              |                           |
| 2                          | chome, Otsu-shi, Shiga-l                    | en           |                           |

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